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REACTIONS OF CHEMICAL WARFARE AGENTS WITH DS2:
PRODUCT IDENTIFICATION BY NMR
II. 2-CHLOROETHYL SULFIDES

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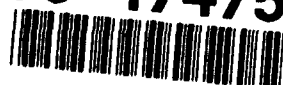
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13. ABSTRACT (Maximum 200 words) ¹³ C NMR spectroscopy was used to monitor the reactions of HD and 2-chloroethyl methyl sulfide (CEMS) with DS2. The 2-chloroethyl sulfides were found to rapidly dehydrohalogenate in DS2, forming their corresponding vinyl elimination products. The presence of water had an adverse effect on the solubility of the 2-chloroethyl sulfides in DS2, and variations in the reaction profile as a function of added water showed that the decreased reactivity of the DS2/H ₂ O solutions results from a change in reaction mechanism. As the amount of H ₂ O increases, the reaction mechanism changes from a rapid elimination to a much slower nucleophilic SN1 process. The major products from the SN1 reaction result from substitution of the chloride in the 2-chloroethyl sulfides by the diethylenetriamine (DETA) in the DS2.				
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PREFACE

The work described in this report was authorized under Project No. 1L161102A71A, Research in CW/CB Defense. This work was started in February 1989 and completed in December 1990.

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*When this work was conducted, ERDEC was known as CRDEC, and the ERDEC authors were assigned to the Research Directorate.

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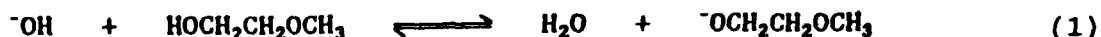
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REACTIONS OF CHEMICAL WARFARE AGENTS WITH DS2:
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II. 2-CHLOROETHYL SULFIDES

1. INTRODUCTION

The U.S. Army standard decontaminating solution, DS2, was developed in the late 1950's and is a general all-purpose decontaminant that reacts rapidly with all known chemical warfare (CW) agents.¹ It is a clear solution consisting of 70% diethylenetriamine (DETA), 28% ethylene glycol monomethyl ether [methyl cellosolve, (MC)], and 2% sodium hydroxide (NaOH) by weight. Each of these components has been shown to play a role in the effective decontamination of the chemical agents.² The DETA has been reported to act as a clathrating agent that sequesters the sodium cation of the NaOH, which frees the hydroxide ion to form a "superbase" (i.e., pH > 14). This superbase then interacts with the MC (equation 1), forming the alkoxide ion (MCO⁻), which acts as the nucleophile in this nonaqueous system. In addition to serving as the source of the nucleophile in the decontamination reactions, the MC also functions as a solvent extender, a mutual solvent for the base, the amine, and the agent. Furthermore, the ratio of MC to DETA has been shown to form an azeotrope, important for keeping the NaOH in solution as the mixture evaporates.^{2,3}



Part I of this series⁴ describes the use of multinuclear NMR to study the reactions of DS2 with the organophosphorus CW agents GA, GB, GD, VX and the V-agent analog O,S-diethyl methylphosphonothiolate (DEMPS). ¹³C and ³¹P NMR were used to identify the products from both primary and secondary reactions and to determine the rates of the secondary reactions and the effect of adding varying amounts of water to the DS2/agent reaction mixtures.

In the second phase of this investigation, ¹³C NMR was used to identify the products from the reaction of DS2 with mustard [(HD), bis(2-chloroethyl)sulfide] and its mono-chloro analog [2-chloroethyl methyl sulfide (CEMS)] and to determine the effect of water on the rates of reaction and on the products formed. This report documents the results of this study.

2. EXPERIMENTAL SECTION

2.1 Materials.

The HD was obtained from the Chemical Agent Standard Analytical Reference Material (CASARM) Program (Lot #HD-U-6216-CTF-N, purity > 95%) and was used as received. The CEMS (Fairfield Chemical Company, Blythewood, SC), purity > 98%, and the DETA (Aldrich, Milwaukee, WI), purity 99%, were also used as received. The DS2 [supplied by Louis Kanaras, Physical Protection Directorate, U.S. Army Chemical Research, Development and Engineering Center (CRDEC)]* was taken from a sealed 1.3-qt can and stored in amber glass bottles under nitrogen until used. Triply distilled water was used to prepare the solutions of DS2 and water.

2.2 Instrumentation.

The ^{13}C NMR spectra were recorded using a Varian VXR-400S superconducting multinuclear Fourier transform (FT) NMR system operating at 100 MHz. Spectra were recorded unlocked at ambient temperature ($\sim 22^\circ\text{C}$) using tetramethylsilane (TMS) in chloroform (CHCl_3) as the external reference. For each sample analyzed, at least 96 transients were accumulated using a pulse width of $10.8\ \mu\text{s}$ ($\sim 74^\circ$), a sweep width of 250 ppm, an acquisition time of 1.6 s, and a pulse delay of 2.5 s. All spectra were accumulated in double precision mode, and full proton WALTZ decoupling was used. Quantitative data were obtained by digital integration of the peak areas of interest and are accurate to $\pm 5\%$.

The ^{13}C NMR parameters for the compounds identified in DS2 are summarized in the Appendix.

2.3 General Procedure.

A weighed amount of substrate was added to a clean, dry 5 mm o.d. Pyrex NMR tube (#507-PP, Wilmad Glass Company, Buena, NJ), and a reacting medium was added to prepare the following solutions:

0.13M HD in DS2
0.15M HD in DS2/ H_2O (50 wt% H_2O)
0.15M CEMS in DS2
0.15M CEMS in DS2/x% H_2O (x = 10, 20, 30, and 49 wt%)
0.50M CEMS in DETA

*Now known as the U.S. Army Edgewood Research, Development and Engineering Center (ERDEC).

The top of the NMR tube was then capped and wrapped with Parafilm, and the tube was shaken to ensure complete mixing. The sample was placed into the spectrometer, and spectra were recorded as required.

3. RESULTS

3.1 Reaction of 2-Chloroethyl Sulfides with DS2.

When CEMS was reacted with DS2 (0.15M in DS2) at ambient temperature ($\sim 20^\circ\text{C}$), the first NMR spectrum obtained (~ 2.5 min after mixing) showed no CEMS remaining. In addition to the resonances for DS2 (see Appendix), three peaks were observed for the CEMS/DS2 reaction product. These resonances are consistent for the elimination product, methyl vinyl sulfide, I (δ_c : CH_3 : 13.4; SCH : 133.7; CH_2 : 108.4). Immediately upon mixing, a white solid precipitated from the solution. Presumably, this solid is NaCl, which forms during the reaction and is insoluble in DS2.

When HD was reacted with DS2 (0.13M in DS2) at ambient temperature, no HD was observed in the first spectrum obtained after mixing (~ 3 min). Two resonances consistent for divinyl sulfide, II (δ_c : CH_2 : 114.7; CH : 130.4) were observed.⁵ There was no evidence in the spectrum for either 2-chloroethyl vinyl sulfide or any of the various HD substitution products.

3.2 Reaction of 2-Chloroethyl Sulfides with DS2 in the Presence of Added Water.

Since the presence of even small amounts of water has been reported to be detrimental to the efficacy of DS2 to decontaminate HD,⁶ the reactions of DS2 with CEMS and HD were reexamined with water present to evaluate its effect on the reaction rates and product distributions.

3.2.1 Reaction of CEMS in DS2 Spiked with Varying Amounts of Water.

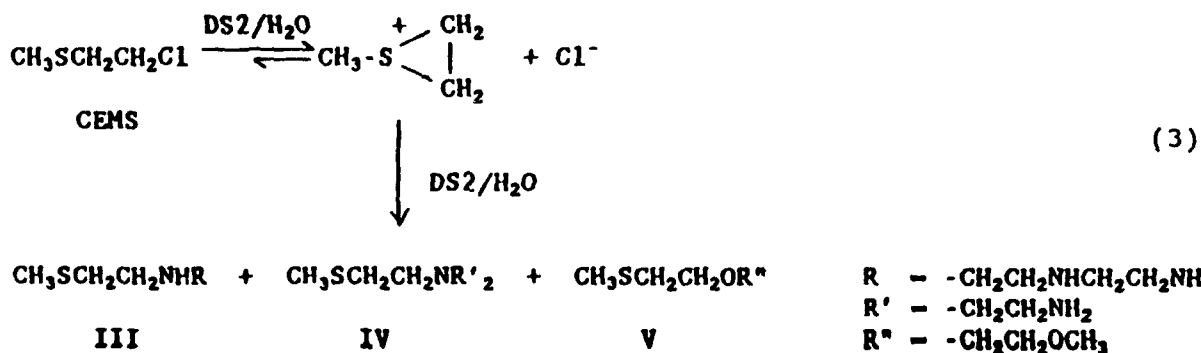
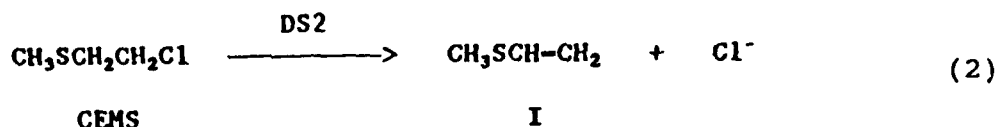
In solutions of DS2 spiked with 10, 20, 30, and 49 wt% water, the solubility of CEMS was greatly diminished. The CEMS appeared to be miscible with the DS2 solutions containing 10 and 20 wt% water. However, it was immiscible with the DS2 solutions containing 30 and 49 wt% water, and two phases were observed. Although the CEMS/DS2/30% H_2O mixture became one phase after several minutes of shaking, it required several hours for the CEMS/DS2/49% H_2O mixture to become homogeneous. In addition, unreacted CEMS was observed in the DS2 mixtures containing 10, 20, and 30 wt% water, as shown in Table 1.

Table 1. Amount of Unreacted CEMS in DS2/H₂O Solutions

[H ₂ O] (wt%)	Time After Mixing (hr)	Amount of CEMS Remaining (mole%)
0	0.05	0
10	1.0	15.5
20	2.0	18.1
30	2.5	14.8
49*	-	-

*Sample 2 phases for several hours. Unreacted CEMS observed in the DS2/H₂O layer during this period.

Because of the reduced solubility and resulting sample inhomogeneity, the CEMS/DS2/H₂O samples were allowed to react overnight at ambient temperature before meaningful spectra were obtained. At 24 hr after mixing, the ¹³C spectra of the reaction mixtures showed four different reaction products present (equations 2 and 3).



The product distribution as a function of the amount of added water is shown in Table 2. The vinyl elimination product, I, was easily identified from its resonances in the unsaturated region of the ^{13}C spectrum (δ_c 109.2 and 133.3) similar to the previous sample, above. Likewise, the MC substitution product V was easily identified from its three equal resonances (δ_c 70.1, 70.4, and 72.0) in the methylene ether region of the ^{13}C spectrum (δ_c 65 to 72).⁷ The identities of III and IV were confirmed by reacting CEMS with DETA, alone. After 66 hr, the ^{13}C spectrum of a 0.5M solution of CEMS in DETA showed that all of the CEMS had reacted to form 88% III from nucleophilic substitution of the chloride by the primary amine function of the DETA (δ_c : CH_3 : 15.4; SCH_2 : 34.5; SCCNCCN : 49.0, 49.6, 49.8; NCCNH_2 : 53.1; NCCNH_2 : 42.1), 9% IV from nucleophilic substitution of the chloride by the secondary amine moiety of the DETA (δ_c : CH_3 : 15.7; SCH_2 : 32.4; SCCN : 54.4; $\text{N}(\text{CCNH}_2)$: 58.1; $\text{N}(\text{CCNH}_2)$: 40.4), and 3% I (δ_c : CH_3 : 13.6; CH_2 : 108.4; CH : 133.7). No resonances at δ_c -23 ppm (CH_3S^+) corresponding to the dimeric sulfonium ions⁸ were observed in any of the CEMS/DS2/ H_2O solutions either at 2 or 24 hr. Thus, it appears that the reactive, cyclic ethylene sulfonium ion intermediate (equation 3) reacted rapidly with the DETA as soon as it was formed.

Table 2. Product Distribution (Mole%) at 24 Hr for 0.50M CEMS in DS2/ H_2O .

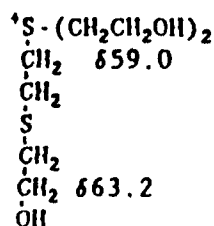
Compound	Wt% H_2O			
	10	20	30	49
I	82.6	57.1	15.2	-
III	13.4	31.8	63.7	76.3
IV	3.9	8.2	17.9	22.9
V	trace	2.9	3.2	0.8

I	$\text{CH}_3\text{SCH}=\text{CH}_2$
III	$\text{CH}_3\text{SCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$
IV	$\text{CH}_3\text{SCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_2$
V	$\text{CH}_3\text{SCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$

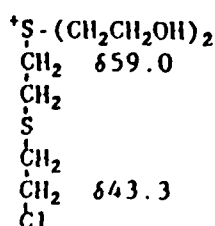
3.2.2 Reaction of HD in DS2 Spiked with Water.

In our laboratory, HD has been found to be much less soluble than CEMS in water and mixed aqueous solvent systems. Because of the solubility problems encountered with CEMS, above, it was considered impractical to try to react HD in the DS2/H₂O solutions since NMR spectra are meaningful only for homogeneous samples. However, one reaction was attempted to see if NMR could distinguish any reaction products between HD and DS2 in the presence of a significant amount of water. Thus, a 0.15M solution of HD in DS2 containing 50 wt% water was prepared and evaluated. As expected, the HD was not miscible with the DS2/50 wt% H₂O, and the sample remained two phases throughout the evaluation period. Consequently, no attempt at quantitation was made. Nevertheless, a ¹³C NMR spectrum of the DS2/H₂O layer was able to yield some information on the reaction products.

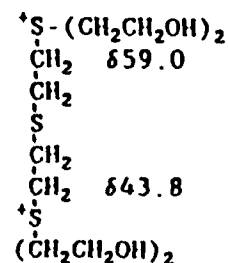
First, as seen with CEMS, no unsaturated carbon resonances were observed, indicating that little, if any, divinyl sulfide, II, or 2-chloroethyl vinyl sulfide was formed. Second, no resonances were observed in the methylene ether region of the ¹³C spectrum, indicating that little, if any, reaction between HD and MC was occurring. Also, there was no evidence for the presence of a -CH₂OH moiety (δ_c ~63 ppm),⁸ indicating little, if any, reaction between HD and hydroxide ion to form either chlorohydrin (2-chloroethyl 2-hydroxyethyl sulfide, HOCH₂CH₂SCH₂CH₂Cl) or thiodiglycol [bis(2-hydroxyethyl)sulfide, (HOCH₂CH₂)₂S]. The lack of a resonance at this position also rules out the presence of the sulfonium ion CH-TG (δ_c 63.2) but not H-TG (δ_c 43.3 and 59.0) nor H-2TG (δ_c 59.0).⁶ The region δ_c 59 to 61 ppm is obscured by the large resonances from the MC in DS2. Consequently, the presence of H-TG and/or H-2TG cannot be completely ruled out.



CH-TG

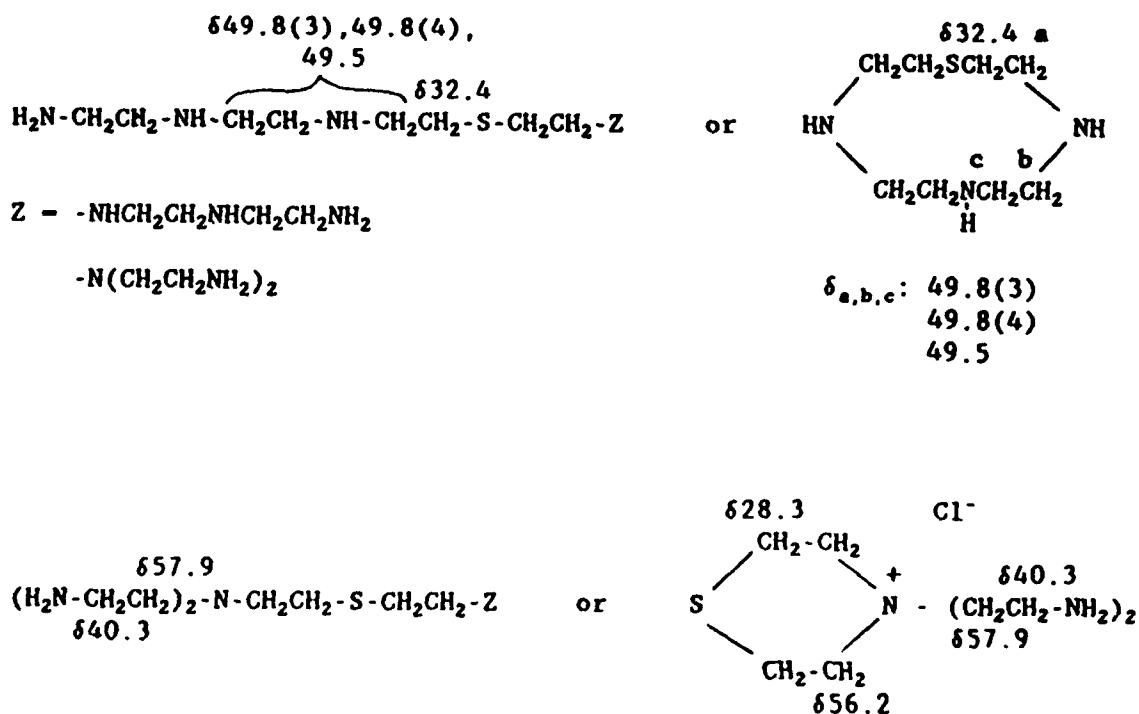


H-TG



H-2TG

All of the product peaks observed in the spectrum of the DS2/H₂O layer appeared to result from the reaction of HD with the two nitrogen moieties in DETA. Six separate resonances (δ_c 32.7, 32.4, 30.5, 30.4, 30.3, and 28.3) were observed in the -SCH₂ region of the spectrum, indicating that three to six different products had been formed. The three equal resonances observed at δ 49.5, 49.8(3), and 49.8(4) are indicative of the presence of the -SCH₂CH₂NHCH₂CH₂N- moiety (see III, Appendix) and confirm that reaction between HD and the primary amino functions of the DETA is occurring. Similarly, the resonances observed at δ_c 57.9, 56.2, and 40.3 are consistent for the presence of the -SCH₂CH₂N(CH₂CH₂NH₂)₂ moiety (see IV, Appendix), indicating significant reaction between HD and the secondary nitrogen of the DETA. Possible chemical shift assignments for the products from the substitution reactions of HD with DETA are shown below.

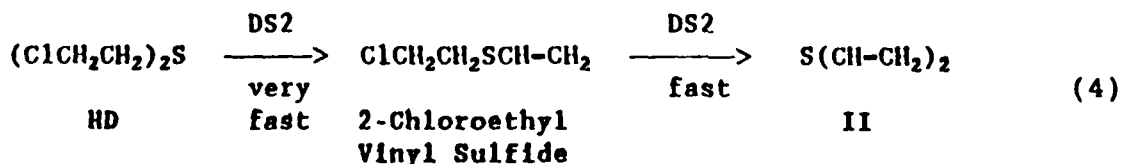


4. DISCUSSION

4.1 Reaction of 2-Chloroethyl Sulfides with DS2.

The only product observed for the reaction of CEMS with neat DS2 was the vinyl elimination product I; for HD with DS2, divinyl sulfide, II, was the only product detected. These results confirm the findings of Davis and co-workers who isolated II from the reaction of HD with DS2 in 31% yield and concluded from their ultraviolet spectrophotometry data that II is the only product formed.⁹ They found that the first elimination reaction

to form 2-chloroethyl vinyl sulfide was too fast to measure and that the second elimination to form II had a $t_{1/2}$ of 2.3 s at 25 °C. They suggested that the overall reaction of HD with DS2 was a clean double elimination process (equation 4). Our results confirm this conclusion since only II was observed in the first NMR spectrum obtained after mixing HD with DS2 (~2 min).



Prior to the study by Davis and co-workers, Jackson¹ tested a solid isolated from the reaction of equal molar quantities of HD and DETA, assuming that it was the same product as that obtained in DS2. That solid was never characterized, but based on the NMR data for the reaction of CEMS in DETA, alone, it was most likely a mixture of substitution products formed from the reaction of the two amino functions in the DETA with HD. Consequently, that solid did not represent the actual DS2/HD reaction product, which has been shown by Davis to be the elimination product II and confirmed by ¹³C NMR in this study.

For elimination reactions, it is generally accepted¹⁰ that there is a spectrum of mechanisms ranging from pure E1, in which the leaving group (i.e., Cl⁻) departs well before the proton, to pure E1cB, in which the proton comes off first; then, sometime later, the leaving group follows. The pure E2 case lies in the middle, with both groups leaving simultaneously. Indeed, most reactions do not follow any of the three cases exactly but fall somewhere in between. Dehydrohalogenation in alcoholic caustic is a characteristic reaction of alkyl halides containing β-hydrogens, and the elimination usually follows an E2 mechanism.¹⁰ Consequently, previous investigators have considered the reaction of HD with DS2 to be a bimolecular E2 process.^{2,9} However, DS2 is an unusual mixture of components, and to determine just where the reaction of HD with DS2 falls within the E1-E2-E1cB spectrum, a study using isotopically labelled compounds is required. Plans are currently underway to study the elimination reactions of various deuterated analogs of HD and CEMS under a variety of conditions to ascertain the stereospecificity of the reaction and to determine any isotope effects on the reaction rates. The latter should give information on the behavior of the various bonds in the transition state, which should lead to a better understanding of the elimination process in 2-chloroethyl sulfides. The results of these investigations will be presented in a future publication.

4.2 Effect of Added Water.

When DS2 is diluted with water, the solubility of the hydrophobic 2-chloroethyl sulfide decreases as the amount of water increases. This lack of solubility adversely affects the decontamination efficacy of DS2 since good solubility is one of the major parameters for successful physical removal of an agent from a surface. On the other hand, decreased solubility does not appear to be the most significant factor in the ability of the DS2/H₂O solutions to detoxify the 2-chloroethyl sulfides. Unreacted CEMS was observed in all of the DS2/H₂O solutions hours after mixing (Table 1). This indicates that the rate of the initial reaction of the 2-chloroethyl sulfides with DS2 decreases sufficiently in the DS2/H₂O solutions to compromise the ability of DS2 to detoxify the agent.

The presence of water in DS2 has two consequences. First, it shifts the equilibrium in equation 1 to the left, thereby decreasing the amount of the very basic alkoxide ion. In addition, the solvating effect of the water on the ions in solution (i.e., RO⁻, HO⁻, and Na⁺) further diminishes the superbase character of the DS2, which benefits any bimolecular elimination process. Second, the presence of water increases the polarity of the medium enhancing reaction mechanisms that involve ionic intermediates. Thus, the presence of water would favor an SN1 substitution reaction mechanism over any elimination mechanism.¹⁰

This is exactly the situation in the DS2/H₂O solutions. Substitution reactions of 2-chloroethyl sulfides follow an SN1 mechanism involving the dissociation of the C-Cl bond with the simultaneous formation of an ethylene sulfonium ion intermediate (see equation 3). These reactions have been found to be relatively slow in mixed aqueous solutions (for 0.17M 2-chloroethyl ethyl sulfide, CEES, in 50% acetone/water at 20 °C, $t_{1/2}$ ~13 min).⁸ On the other hand, the nonaqueous elimination reaction is quite fast as previously described. Table 2 shows that as more water is added to the DS2, more substitution products are formed. This indicates that the rate of the elimination reaction is decreasing; whereas, the rate of the SN1 substitution reaction is increasing until 35-40 wt% water is present. At this point, the medium is such that substitution is completely favored over elimination (see the figure).

Contrary to the prediction by Small³ that diluting DS2 with H₂O would give the HD hydrolysis products (i.e., chlorohydrin and thiodiglycol), no evidence for reaction of either CEMS or HD with hydroxide ion was observed. Since the substitution reactions of 2-chloroethyl sulfides follow an SN1 mechanism with the rate-determining step being the formation of the ethylene sulfonium ion,⁸ both the concentration of the nucleophile and its strength are the controlling factors that determine the product

distribution. Thus, it is not surprising that the DETA substitution products predominate (>99% for CEMS in DS2/49 wt% H₂O) since DETA is the most abundant, strong nucleophile present and that the ratio of the two DETA substitution products III and IV remains the same for all of the DS2/H₂O solutions [78:22 (\pm 1)] as shown in Table 2.

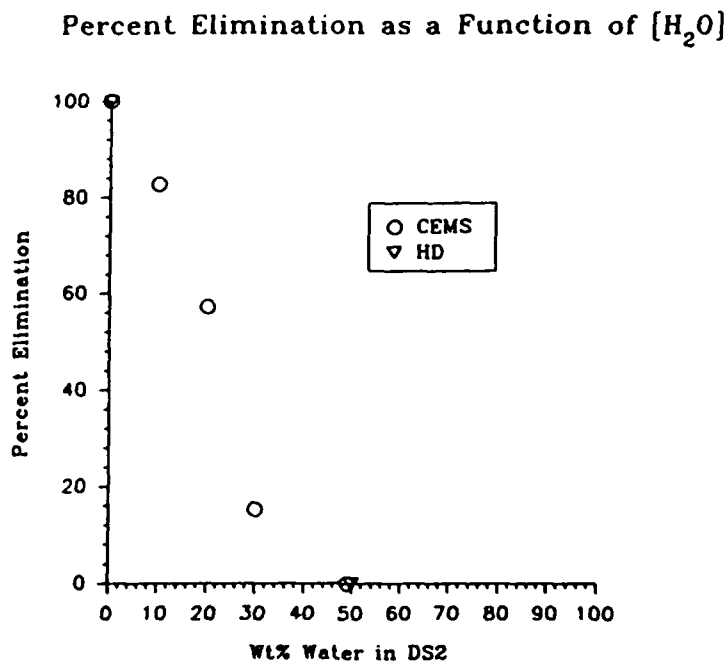


Figure. Percentage of Reaction by Elimination as a Function of the Amount of Added Water in DS2 for CEMS and HD

5. CONCLUSIONS

2-Chloroethyl sulfides are rapidly dehydrohalogenated in DS2 to form their corresponding vinyl elimination products. HD, itself, undergoes a clean double elimination in less than 2 min to form divinyl sulfide as the only product of the reaction.

As water is added to DS2, the solubility of the 2-chloroethyl sulfides is diminished. More importantly, the ability of the DS2 to detoxify the 2-chloroethyl sulfides is significantly reduced. This results from a change in reaction mechanism, from elimination (rapid in basic, nonaqueous media) to SN1 (slow in mixed aqueous systems) as the concentration of water increases. The major products observed from the SN1 reaction of 2-chloroethyl sulfides in DS2/H₂O (up to 50 wt% H₂O) are the products formed from the substitution of the chloride by either the primary or secondary amino moiety of the diethylenetriamine (DETA) component of DS2. No hydrolysis products are formed.

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APPENDIX

REPRESENTATIVE ^{13}C NMR PARAMETERS FOR COMPOUNDS IDENTIFIED IN DS2

Compound	Solvent	δ_{C} , ppm
CEMS	DS2/30 wt% H_2O	CH_3 : 15.4; SCH_2 : 36.5; CH_2Cl : 44.2.
I	DS2/30 wt% H_2O	CH_3 : 13.5; SCH : 133.3; CH_2 : 109.2.
DETA	DS2	H_2NCH_2 : 42.1; HNCH_2 : 53.0.
MC	DS2	CH_3 : 58.6; OCH_2 : 75.3; CH_2OH : 60.5.
HD	Neat	SCH_2 : 35.8; CH_2Cl : 45.0.
II	DS2	SCH : 130.4; CH_2 : 114.7.
III	DS2/30 wt% H_2O	CH_3 : 15.1; SCH_2 : 33.5; SCCNCCN : 48.3, 48.6, 48.9; NCCNH_2 : 52.2; NCCNH_2 : 41.2.
IV	DS2/30 wt% H_2O	CH_3 : 15.5; SCH_2 : 31.9; CH_2N : 53.9; $\text{N}(\text{CCNH}_2)$: 56.9; $\text{N}(\text{CCNH}_2)$: 39.4.
V	DS2/30 wt% H_2O	CH_3 : 15.7; SCH_2 : 33.8; SCCOCCO : 70.1, 70.4, 72.0; CH_3O : 58.2.